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A THERMAL METHOD FOR PRODUCTION OF ZIRCONIUM DIOXIDE MICROFIBERS

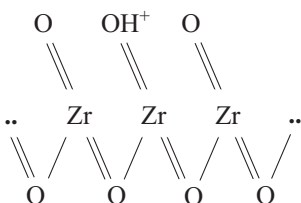
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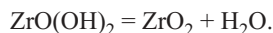
A method for production of ZrO_2 microfibers by precipitation of zirconium hydroxide from zirconate-bearing aqueous solutions and subsequent calcination to obtain dioxide is proposed. A laboratory technological scheme for producing zirconium dioxide microfibers is developed.

It is known [1] that zirconium hydroxide precipitates in the pH range of 1.9–2.5. If hydroxide precipitates in the crystalline form, low-water hydroxides contain up to 65–70% ZrO_2 , which is the nearest to the chemical formula $\text{ZrO}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. By modifying the precipitation parameters, it is possible to control the size of microfibers (Fig. 1).

The structural formula of zirconium hydroxide is a polymer based on ZrO_2 fragments linked by the donor-acceptor bond and forming a skeleton:



The aggregates besides the coordination-fixed water retain a certain number of water molecules by means of physical adsorption. In aging they become larger, lose water, and gradually transform into amorphous dioxide. Zirconium dioxide in heating transforms into oxide:



The heating rate determines the subsequent structural modification of ZrO_2 . Heating in the temperature interval of 430–470°C leads to the formation of the tetragonal modification and at a temperature above 600°C the tetragonal modification transforms into the monoclinic one [1].

The investigation of regularities of decomposition of zirconium hydroxide is needed to determine the process parameters, under which it transforms into dioxide without losing

the shape of microfibers. The kinetics of decomposition of zirconium hydroxide microfibers was studied in an immobile layer at a constant temperature modifying the duration of its existence in the heating zone or modifying the heating temperature under a constant heating duration. Decomposition of hydroxide was monitored by periodic weighing on a torsion scale.

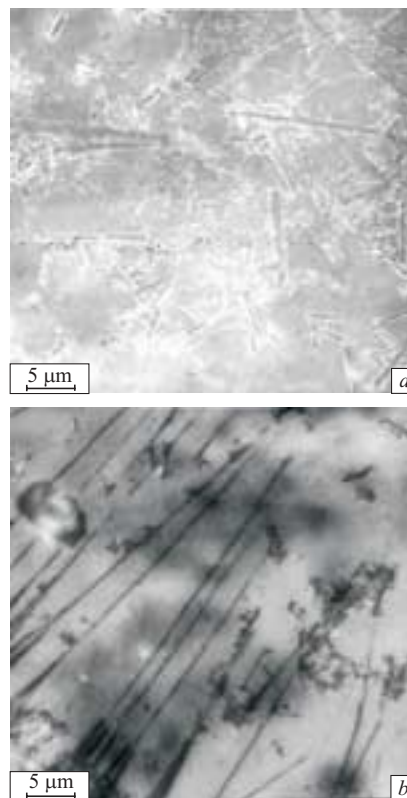


Fig. 1. Electron microscope studies of zirconium dioxide fibers: *a* and *b*) precipitation at 110 and 90°C, respectively.

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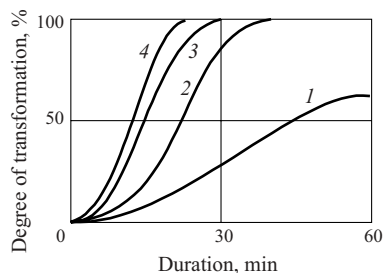


Fig. 2. Dependence of the degree of transformation of zirconium hydroxide into dioxide depending on treatment duration at temperatures of 400 (1), 450 (2), 500 (3), and 600°C (4).

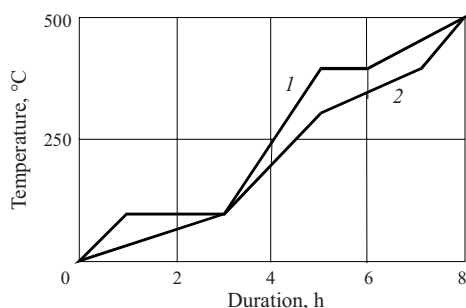


Fig. 3. Modes of heat treatment of zirconium hydroxide.

It can be seen in Fig. 2 that full transformation can be reached faster at the temperature of 600°C. Experimental results were processed using the kinetic equation of a decreasing volume:

$$1 - (1 - \alpha)^{1/n} = k\tau,$$

where α is the degree of transformation; k is the reaction rate constant; τ is the duration of transformation; $n = 3$ in the decreasing volume equation [2].

The experimental data indicate that at 600°C full transformation can be achieved faster. However, it is essential to conduct the process in such a way as to prevent full destruction of the microfibers. The obtained results were processed according to the above equation, after which the process activation energy was calculated using the Arrhenius equation and found to be equal to 2.8 kJ/mole. This value indicates that the limiting stage of the process is external diffusion [1], and this means that the process rate is determined by the rate of water removal from the space between the crystallites. This is the slowest stage in the immobile layer of materials, and the transformation process takes several hours.

To preserve the shape of microfibers, heating has to be effected in several stages. According to the data obtained on a Paulik – Paulik – Erdey derivatograph, it was found that zirconium hydroxide transforms into oxide at a temperature of 407°C. The assumption was made that at the first stage intercrystallite and adsorption water has to be removed at a temperature below 103°C, and in the second stage crystalli-



Fig. 4. Fragmentation of microfiber of zirconium hydroxide.

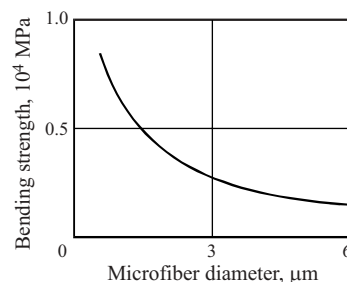


Fig. 5. Dependence of bending strength on the microfiber diameter.

zation water is removed at a temperature below 410°C. Two heating modes are indicated in Fig. 3: mode 1) the fibers retain their shape; mode 2) the fibers partly or completely disintegrate. It was registered that disintegration of initial microfiber is accompanied with loss of water layer by layer, fragmentation of the fiber, and subsequent disintegration. (Fig. 4).

It can be seen from Fig. 3 (mode 1) that slow heating takes place at the first stage. Then for 2 h the temperature does not vary, and during the next 3 h the temperature increases to 410°C. An exposure takes place at this stage, and then the temperature grows to 500°C. Zirconium dioxide fibers of the tetragonal modification originate as a consequence of such thermal treatment, which was confirmed by x-ray phase analysis using a DRON-3 instrument. The thermal conductivity of the fibers amounted to 0.01 – 0.04 W/(m · K). Mode 2 differed from mode 1 in that exposure at 100°C did not happen, and therefore the degree of destruction of the fibers was higher.

Figure 5 shows the dependence of the bending strength of microfiber on its diameter. It can be seen that the strength of the microfibers is sufficient for using them in composite materials. To produce microfiber in required quantities, a technology has to be developed that is based on traditional processes and can be implemented using known chemical equipment.

Figure 6 shows a laboratory technological scheme for production of zirconium dioxide microfibers. According to this scheme, a zirconate solution fed from container 1 and (NH₂)₂CO from container 2 arrive at the reactor 3, where they are heated to a temperature of 90°C. After 30 min, the

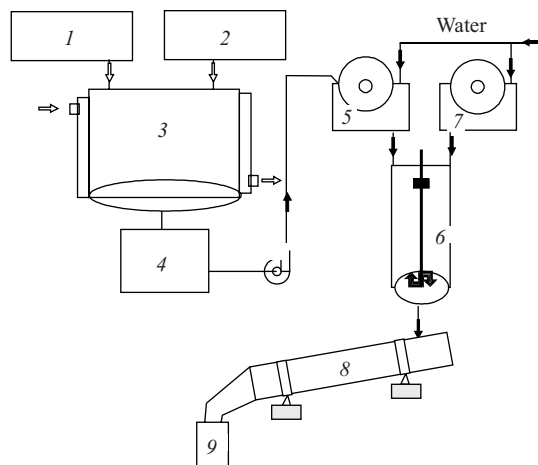


Fig. 6. Laboratory technological scheme for production of zirconium dioxide microfibers.

mixture that had reacted is fed into a holding tank 4. After settling, 2/3 of the clarified mother solution is taken out for utilization, and the remaining suspension is fed to the vacuum filter 5. The filtered microfibers are fed into a repulper 6, where they are washed and again filtered on the vacuum filter 7. After the second filtering, fibers are sent into the calcination furnace 8 with several heating zones. After calcination in the furnace, microfibers of ZrO_2 arrive at the tank 9.

The proposed technological scheme is a batch process of producing microfibers of ZrO_2 (Fig. 7).

Thus, the production of zirconium dioxide microfibers is possible in principle, but the total duration of the process is



Fig. 7. Electron-microscope photos of zirconium dioxide microfiber after heat treatment.

about 10 h, and the heat treatment of zirconium hydroxide takes about 8 h. The production of ZrO_2 microfibers is a batch process. Accordingly, it is necessary to develop a technology for continuous production of zirconium hydroxide microfibers and accelerate the decomposition of hydroxide using more intense mass-transfer processes, such as a “boiling layer” or constrained fall of the solid phase in an ascending gas flow.

REFERENCES

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